REPORT 1065

CORRELATION OF PHYSICAL PROPERTIES WITH MOLECULAR STRUCTURE FOR SOME DICYCLIC HYDROCARBONS HAVING HIGH THERMAL-ENERGY RELEASE PER UNIT VOLUME—2-ALKYLBIPHENYL AND THE TWO ISOMERIC 2-ALKYLBICYCLOHEXYL SERIES [1]

By Irving A. Goodman and Paul H. Wise

SUMMARY

Three homologous series of related dicyclic hydrocarbons are presented for comparison on the basis of their physical properties, which include net heat of combustion, density, melting point, boiling point, and kinematic viscosity. The three series investigated include the 2-n-alkylbiphenyl, 2-n-alkylbicyclohexyl (high boiling), and 2-n-alkylbicyclohexyl (low boiling) series through C_{16}, in addition to three branched-chain (isopropyl, sec-butyl, and isobutyl) 2-alkylbiphenyls and their corresponding 2-alkylbicyclohexyls. The physical properties of the low-boiling and high-boiling isomers of 2-sec-butylbicyclohexyl and 2-isobutylbicyclohexyl are reported herein for the first time.

Comparisons are made on the following bases:

(1) As members of a homologous series in which the compounds have similar structures and differ in molecular weight

(2) As isomers with the same molecular weight and molecular formula but different molecular structures due to branching of the side chain or to geometric isomerism

(3) As compounds with the same carbon skeleton but different molecular formulas due to hydrogenation of the aromatic rings.

INTRODUCTION

In evaluating hydrocarbons for their suitability as fuels for high-speed aircraft, several important properties must be considered. Among these properties are net heat of combustion per unit volume and per unit weight, density, melting point, boiling point, and viscosity. An investigation of the effect of change in molecular structure on these properties should prove helpful in the selection of hydrocarbons possessing the most desirable properties.

A typical aircraft fuel in current use is described by MIL–F–5624 (grade JP-3) specifications in reference 1. Fuels purchased under these specifications from five different sources for use at the NACA Lewis laboratory had values of net heat of combustion ranging from 894,000 to 925,000 Btu per cubic foot (average, 911,000 Btu/cu ft) and 18,480 to 18,690 Btu per pound (average, 18,580 Btu/lb). The net heat of combustion of biphenyl is 1,096,000 Btu per cubic foot, a value which is 20 percent greater than the average JP-3 fuel value, but only 16,850 Btu per pound, or about 9 percent less than the corresponding JP-3 value. A fuel that would deliver the maximum heat energy per unit volume without appreciably sacrificing heat release per unit weight would extend the flight range of volume-limited aircraft. Biphenyl is unsuitable for use as a liquid fuel because of its low heat release per pound and its relatively high melting point (69.2° C). Lower melting points could be expected if alkyl groups were introduced in the 2-position of biphenyl. Moreover, this result could possibly be achieved without appreciably affecting the heat of combustion per unit volume and per unit weight. The addition of alkyl groups to biphenyl would, however, affect other properties, such as boiling point and viscosity, and therefore an examination of these effects is also of considerable importance.

A previous report (reference 2) correlated the molecular structure and physical properties of some hydrocarbons in the 2-*n*-alkylbiphenyl, 1,1-diphenylalkane, α,ω-diphenylalkane, 1,1-dicyclohexylalkane, and α,ω-dicyclohexylalkane series. The 2-*n*-alkylbiphenyl series originally reported in reference 2, which included methyl, ethyl, propyl, and butyl as the substituent alkyl groups, is again presented for further comparison. In addition, three branched-chain 2-alkylbiphenyls are presented; namely, 2-isopropylbiphenyl, 2-*sec*-butylbiphenyl, and 2-isobutylbiphenyl, along with the two isomeric series of 2-alkylbicyclohexyls which are obtained by hydrogenation of the 2-alkylbiphenyls. Inasmuch as many properties must be considered in selecting a fuel, it seemed advisable to study the saturated or hydrogenated derivatives of the 2-alkylbiphenyls in order to determine accurately the property changes caused by hydrogenation. Hydrogenation of each of the 2-alkylbiphenyls to produce the corresponding 2-alkylbicyclohexyls yields mixtures of geometric isomers that are separable by fractional distillation; these compounds are herein designated as the low-boiling and high-boiling isomers because definite assignment of *cis* or *trans* configuration cannot be made at this time.

Comparisons are made on the same bases as those used in reference 2, as follows:

(1) As members of a homologous series in which the compounds have similar structures and differ in molecular weight

(2) As isomers with the same molecular weight and molecular formula but different molecular structures due to branching of the side chain or geometric isomerism

(3) As compounds with the same carbon skeleton but different molecular formulas due to hydrogenation of the aromatic rings.

[1] Supersedes NACA TN 2419, "Correlation of Physical Properties with Molecular Structure for Dicyclic Hydrocarbons. II—2-Alkylbiphenyl and the Two Isomeric 2-Alkylbicyclohexyl Series" by Irving A. Goodman and Paul H. Wise, 1951.

MATERIALS AND PROCEDURE

The syntheses and physical properties of all of the hydrocarbons examined herein, with the exception of the isomeric pairs of 2-*sec*-butylbicyclohexyl and 2-isobutylbicyclohexyl, have been previously reported (reference 3). These two pairs were synthesized and purified in the same manner as the other 2-alkylbicyclohexyls, and their physical properties are reported herein for the first time. Fractionation of the hydrogenation product of 2-*sec*-butylbiphenyl failed to produce the usual separation into two fractions, each having a constant index of refraction, and refractionation of the two halves of the distillate did not improve the product. Because in this case (and in other cases in which the material would not crystallize) selection of pure isomers could not be made on the basis of melting point, the other properties were determined for each isomer on the portions of distillate having the most nearly constant density values.

Physical constants were determined only after every precaution had been taken to ascertain that the high purity essential for the accurate study of properties had been attained. In general, the purity of the hydrocarbons synthesized was estimated to be of the order of 99 mole percent or higher.

The properties of the 2-alkylbiphenyls (table I) and those of the 2-alkylbicyclohexyls (table II) were determined as follows:

The time-temperature melting curves were determined with a platinum resistance thermometer and a G–2 Mueller bridge with accessory equipment and by methods described in reference 4; the melting points were determined from the curves according to the graphical method described in reference 5. Densities were determined by use of a gravimetric balance according to the method of reference 6, and indexes of refraction were measured with a Bausch & Lomb precision oil-model refractometer. The boiling points were determined by use of a platinum resistance thermometer in an apparatus modified from that described in reference 7. The system was pressurized with dry air from a surge tank and held at constant pressure by adjusting a continuous bleed. The kinematic viscosities were determined in viscosimeters that had been calibrated with National Bureau of Standards viscosity samples H–5, H–7, D–7, or L–17. The A. S. T. M. procedure of reference 8 was followed. The net heats of combustion were determined according to reference 9 in an oxygen-bomb calorimeter that had been calibrated on Bureau of Standards benzoic acid.

The magnitude of the uncertainties is estimated as follows: melting point, 0.02° C; density, 0.00005 gram per milliliter; refractive index, 0.0002; boiling point, 0.1° C; kinematic viscosity, 0.5 percent of determined value relative to 1.007 centistokes for water at 20° C; and net heat of combustion, 200 Btu per pound, which is equivalent to 20 to 30 kilogram-calories per mole for these compounds.

The precision of measurements is: melting point, ±0.003°C; density, ±0.00002 to ±0.00003 gram per milliliter; refractive index, ±0.0001; boiling point, ±0.04° C; kinematic viscosity, 0.2 percent of determined value; and net heat of combustion, ±60 Btu per pound.

DISCUSSION OF RESULTS

The effect of change in molecular structure on the various physical properties is discussed in this section. For convenience, the normal-chain hydrocarbons are considered first, and the branched-chain hydrocarbons are discussed subsequently.

2-*n*-ALKYLBIPHENYLS AND 2-*n*-ALKYLBICYCLOHEXYLS

Net heat of combustion.—The net heat of combustion per unit volume is plotted in figure 1 against molecular structure for the three homologous series. The net heat of combustion per unit volume is a maximum for biphenyl, parent member of the 2-*n*-alkylbiphenyl series, and decreases with the addition of each carbon atom to lengthen the side chain in the 2-position. In the case of the two isomeric series of 2-*n*-alkylbicyclohexyls, no significant trend is observed. Within the limits of accuracy of the determinations, the heats of combustion per unit volume within either series are relatively constant. Because of the higher densities in the high-boiling series (fig. 2), the net heats of combustion per unit volume in this series are consistently higher than those of the corresponding members of the low-boiling series.

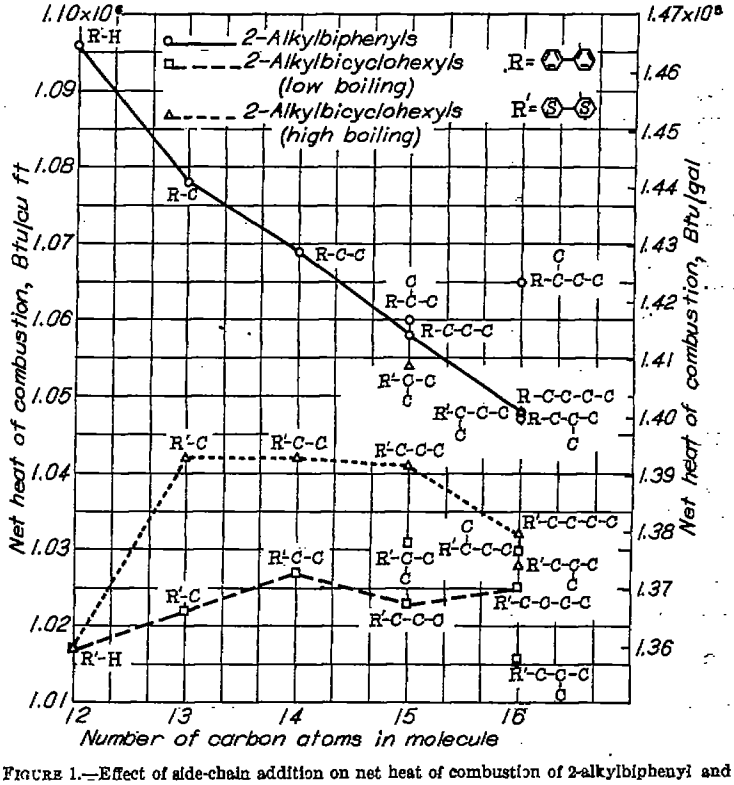


FIGURE 1.—Effect of side-chain addition on net heat of combustion of 2-alkylbiphenyl and 2-alkylbicyclohexyl hydrocarbons.

The densities of the 2-*n*-alkylbiphenyl and 2-*n*-alkylbicyclohexyl series are plotted in figure 2; the marked similarity between figures 1 and 2 indicates that the density of a compound is the important factor in determining the relative heats of combustion per unit volume for members of a homologous series.

On a weight basis, the trends in heat of combustion are somewhat different. In this case, the net heat of combustion is at a minimum for biphenyl (table I) and increases slightly with the successive addition of each carbon atom to lengthen

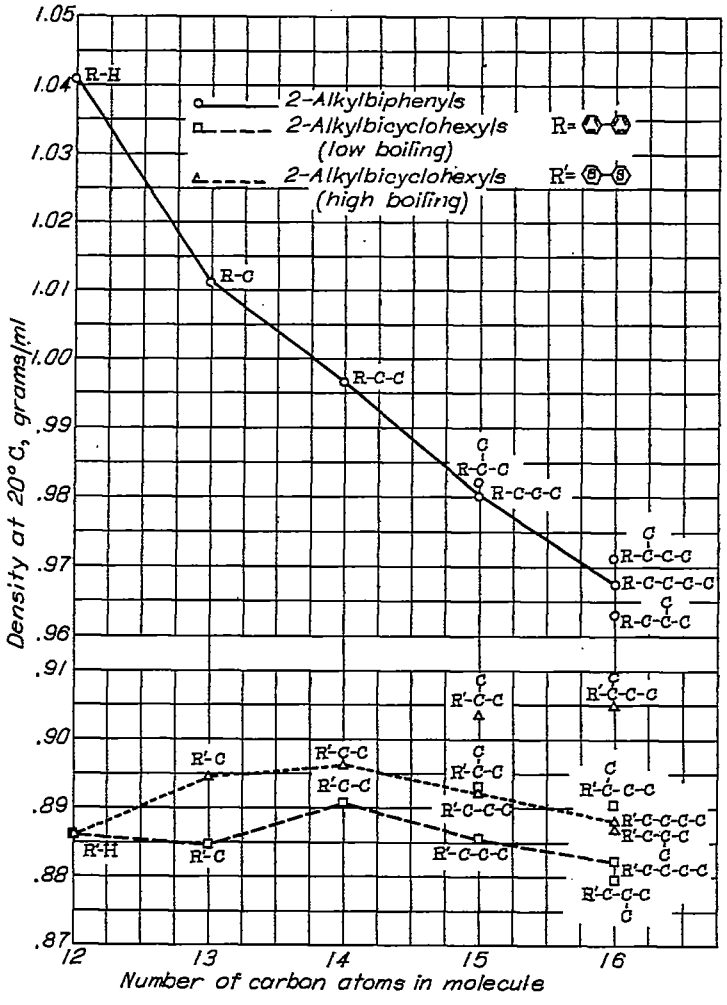


FIGURE 2.—Effect of side-chain addition on density of 2-alkylbiphenyl and 2-alkylbicyclohexyl hydrocarbons.

the side chain. The 2-alkylbicyclohexyls show a relatively constant value for this property within the limits of experimental error. This behavior might be expected inasmuch as the hydrogen-carbon ratio remains practically constant for these series; the addition of a CH_2 group to the side chain has a negligible effect on the over-all hydrogen-carbon ratio.

Hydrogenation of the rings caused decreases in net heat of combustion per unit volume (fig. 1) of the 2-alkylbicyclohexyls from the 2-alkylbiphenyls, ranging from 1.5 percent for 2-butylbicyclohexyl (high boiling) to 5.2 percent for 2-methylbicyclohexyl (low boiling) and 7.2 percent for bicyclohexyl. Hydrogenation of the aromatic rings caused increases in net heat of combustion per pound over the corresponding 2-alkylbiphenyl compounds, ranging from 7.1 percent for 2-butylbicyclohexyl (low boiling) to 9.1 percent for 2-methylbicyclohexyl (high boiling) and 9.2 percent for bicyclohexyl.

The 2-*n*-alkylbiphenyls (including biphenyl) had values of net heat of combustion ranging from 1,048,000 to 1,096,000 Btu per cubic foot and averaging 1,070,000 Btu per cubic foot or 17 percent higher than the average JP–3 fuel value. Biphenyl, the parent member of the series, had the highest net heat of combustion, 1,096,000 Btu per cubic foot, which is 20 percent higher than the JP–3 fuel average. The 2-*n*-alkylbicyclohexyls (including bicyclohexyl) had values ranging from 1,017,000 to 1,042,000, averaging 1,030,000 Btu per cubic foot, still about 13 percent higher than the average JP–3 fuel value. Bicyclohexyl itself had a net heat of combustion of 1,017,000 Btu per cubic foot, the lowest of all three series.

On a weight basis, the 2-*n*-alkylbiphenyls had values of net heat of combustion ranging from 16,850 to 17,375 Btu per pound and averaging 17,160 Btu per pound or 7.6 percent lower than the average JP–3 fuel value. The 2-*n*-alkylbicyclohexyls had values ranging from 18,400 to 18,675 Btu per pound, averaging 18,570 Btu per pound, which corresponds very closely to the average JP–3 fuel value.

As would be expected, on the basis of kilogram-calories per mole, the corresponding members of the two isomeric series of alkylbicyclohexyls have net heats of combustion very nearly equal to each other and 13 to 16 percent higher than the corresponding alkylbiphenyl compounds. In each series, the net heat of combustion increases about 150 kilogram-calories per mole with the addition of each carbon atom to the side chain.

Melting point.—The melting points of the high-boiling 2-*n*-alkylbicyclohexyl series and the 2-*n*-alkylbiphenyl series are plotted in figure 3. The melting points of biphenyl and 2-methylbiphenyl are higher than the corresponding bicyclohexyl compounds, but the remainder of the *n*-alkylbiphenyls have melting points lower than the corresponding

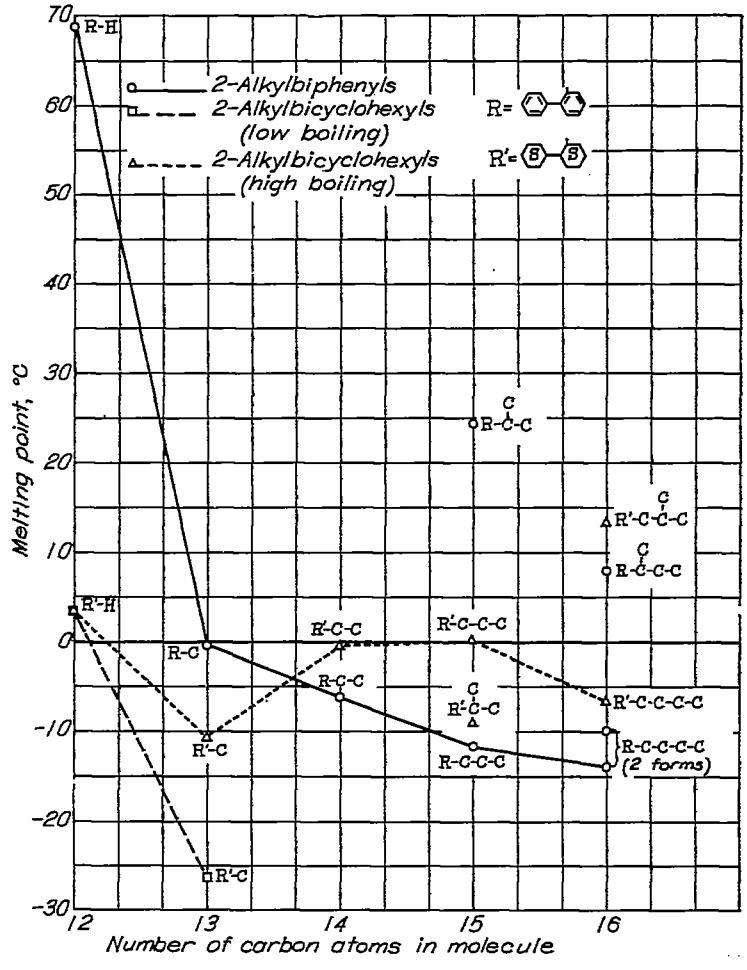


FIGURE 3.—Effect of side-chain addition on melting point of 2-alkylbiphenyl and 2-alkylbicyclohexyl hydrocarbons.

n-alkylbicyclohexyls. As indicated in table II, 2-methylbicyclohexyl (low boiling) was the only member of the low-boiling series that could be crystallized, and its melting point was the lowest among the compounds reported.

The addition of each carbon atom to the biphenyl side chain had the effect of progressively lowering the melting point (although the higher-melting form of 2-butylbiphenyl, which showed two crystalline modifications, has a higher melting point than the previous member, 2-propylbiphenyl). However, this apparently consistent downward trend with increased alkyl chain length should not be accepted as a basis for predicting melting points, for this behavior is not at all general. The melting points for the 2-*n*-alkylbicyclohexyl (high boiling) series show a typical, more random trend.

Boiling point.—The boiling points of members of the three series are plotted in figure 4. For all three series, the boiling point increased regularly with increased alkyl chain length. Increasing the length of the alkyl chain attached to bicyclohexyl causes a greater rate of increase of boiling point for both the high- and low-boiling series than for the corresponding alkylbiphenyl series. Starting with the C_{14} hydrocarbons, the 2-*n*-alkylbiphenyls have boiling points that are progressively lower than those of the corresponding high- and low-boiling alkylbicyclohexyls with each addition of a carbon atom to the chain.

The differences between the boiling points of corresponding high- and low-boiling isomers decrease as the alkyl chain length is increased.

Viscosity.—The kinematic viscosities for the three series at four temperatures are plotted in figure 5. Consistent increase in viscosity with increase in chain length is observed for all the series at all temperatures. With each successive addition of a carbon atom to the alkyl chain, the rate of increase in viscosity becomes greater as the temperature is lowered. For example, at 98.9° C there is a viscosity increase of only 44 percent from 2-methylbicyclohexyl (low boiling) to 2-butylbicyclohexyl (low boiling), but at 0° C, the corresponding increase amounts to 380 percent.

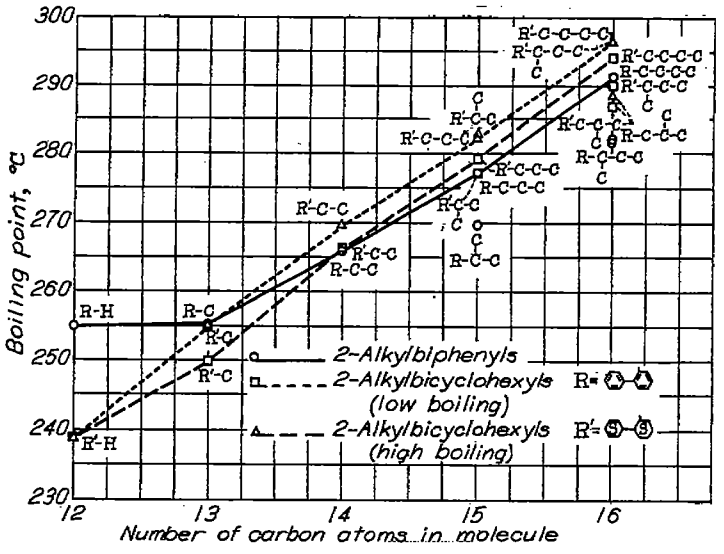


FIGURE 4.—Effect of side-chain addition on boiling point of 2-alkylbiphenyl and 2-alkylbicyclohexyl hydrocarbons.

The viscosities of the 2-alkylbiphenyls are in general lower than those of the corresponding 2-alkylbicyclohexyls, with the exception of 2-methylbiphenyl, which at 0° C has a viscosity higher than either isomer of 2-methylbicyclohexyl and, at 37.8° C, is slightly higher than the low-boiling isomer.

Kinematic viscosities are also plotted in figure 6 (a) on A. S. T. M. Standard Viscosity-Temperature Charts D341–43D (low range) in order to illustrate more clearly the effect of temperature on the viscosity of the various hydrocarbons. Each figure compares the three hydrocarbons having the same carbon skeleton. The A. S. T. M. slopes, which express the rate of change of viscosity with temperature, were calculated according to reference 10 and are tabulated for the *n*-alkyl hydrocarbons as follows:

Alkyl substituent	A. S. T. M. slope		
	Biphenyl compound	Bicyclohexyl compound	
		Low boiling	High boiling
2-Methyl	1.04	0.85	0.82
2-Ethyl	.97	.89	.87
2-Propyl	.98	.93	.91
2-Butyl	.96	.93	.91

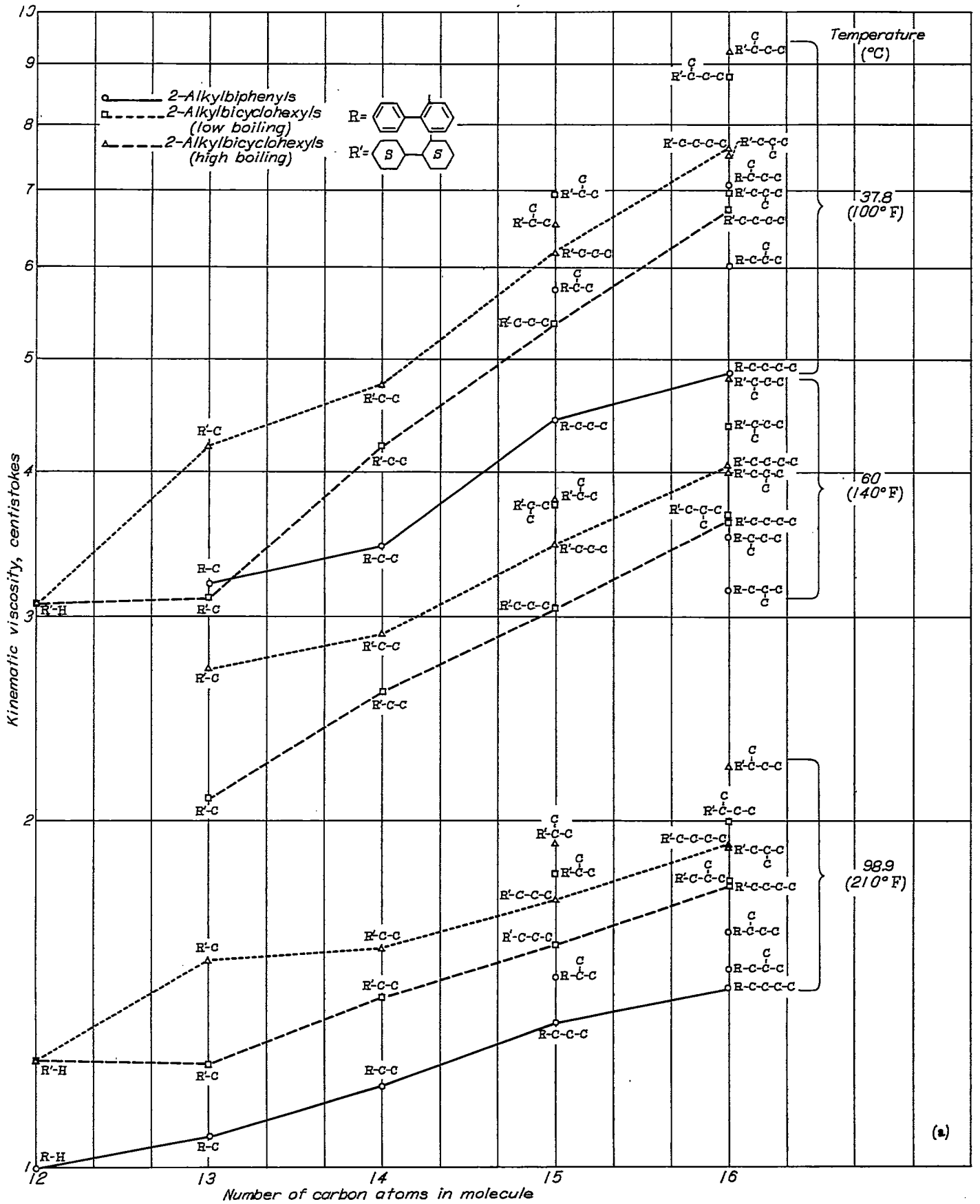
In all cases, it is observed that the slope, or the rate of change of viscosity with temperature for compounds with a given number of carbon atoms, is greatest for the biphenyl hydrocarbon and least for the high-boiling bicyclohexyl compound. The degree of convergence (or the difference) between the slope of a biphenyl hydrocarbon and that of its corresponding bicyclohexyl compound decreases as the length of the side chain increases. The compound whose viscosity shows the least temperature sensitivity in this group is the high-boiling isomer of 2-methylbicyclohexyl, whereas 2-methylbiphenyl shows the greatest sensitivity.

BRANCHED-CHAIN 2-ALKYLBIPHENYLS AND 2-ALKYLBICYCLOHEXYLS

Because of the limited number of branched-chain hydrocarbons reported herein, no very positive correlations can be drawn. Certain interesting observations may be made, however, in comparing the properties of these compounds with their straight-chain counterparts.

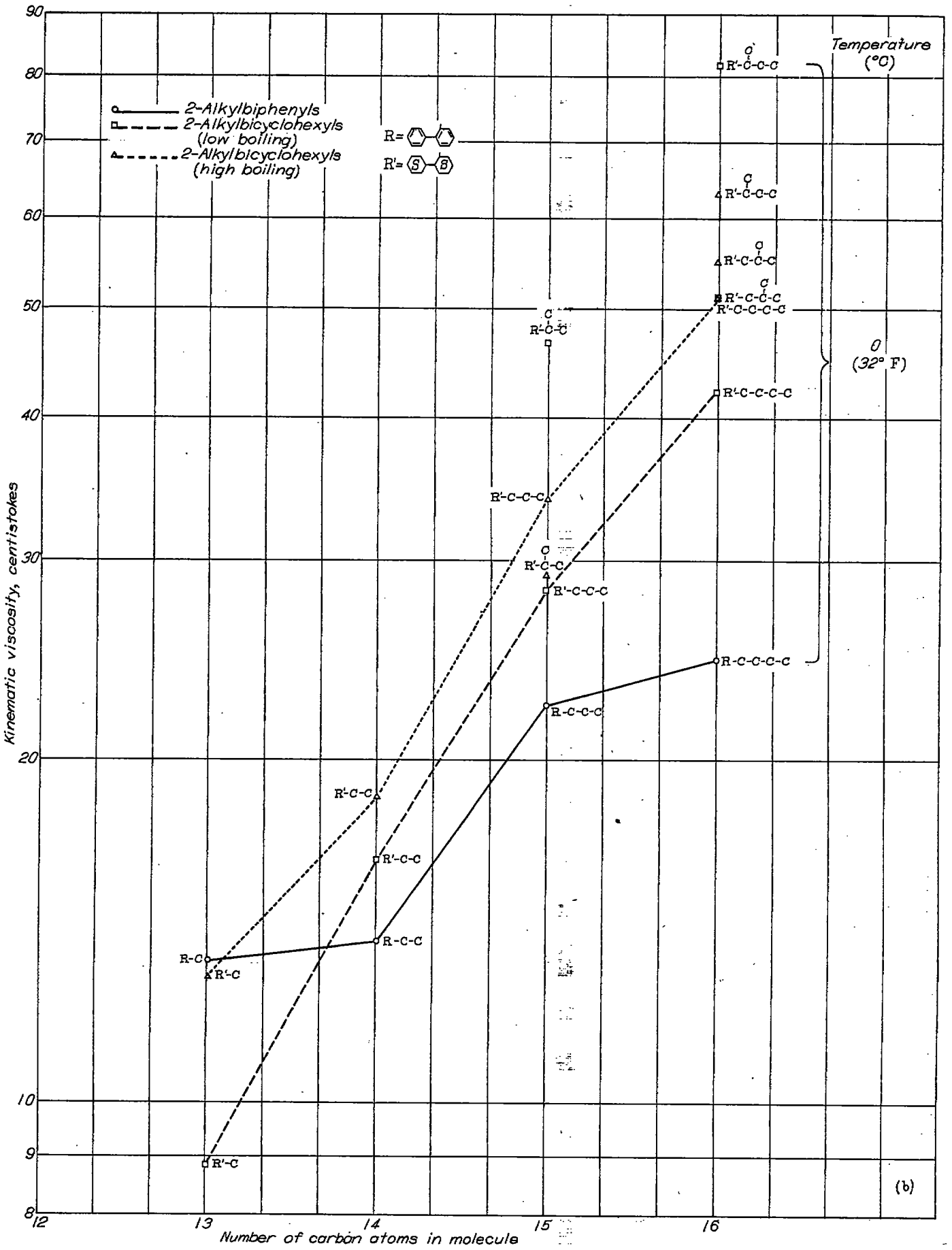
As would be expected, branching the alkyl chain has no appreciable effect on the net heat of combustion in kilogram-calories per mole. The maximum change, which was about 1 percent and within the limits of experimental error, was observed in comparing 2-*sec*-butylbiphenyl with 2-*n*-butylbiphenyl, the branched-chain compound showing the slightly higher value. Because of the differences in density (fig. 2), the net heats of combustion per unit volume of the branched-chain hydrocarbons differ from those of the corresponding straight-chain hydrocarbons.

With regard to melting point, figure 3 shows that branching of the alkyl chain causes an increase over the corresponding straight-chain compound in three of the four cases observed; the exception was 2-isopropylbicyclohexyl (high boiling), which melted about 9° C lower than the high-boiling isomer of 2-propylbicyclohexyl.



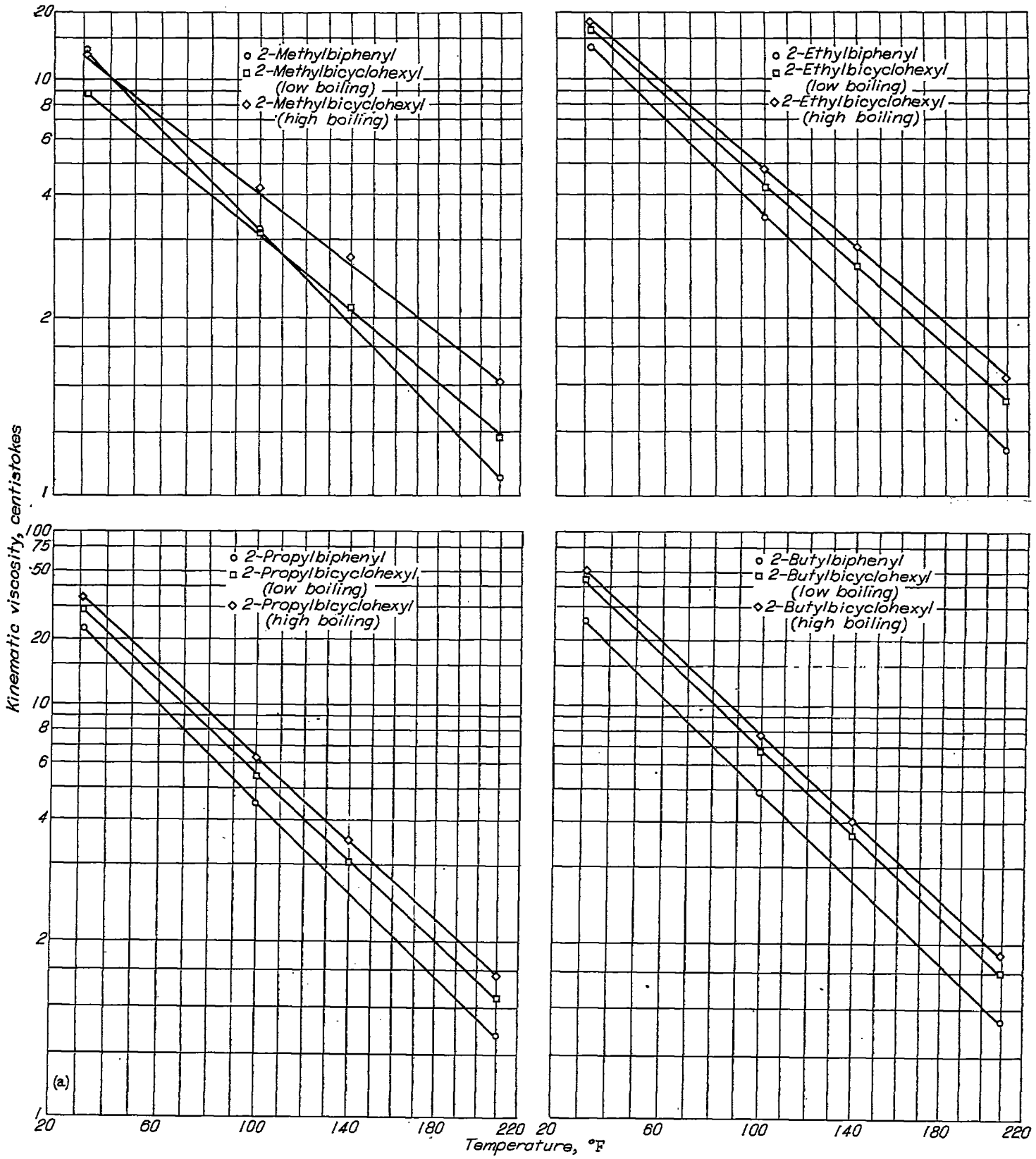
(a) Temperatures, 37.8°, 60°, and 98.9° C.

FIGURE 5.—Effect of side-chain addition on viscosity of 2-alkylbiphenyl and 2-alkylbicyclohexyl hydrocarbons at various temperatures.



(b) Temperature, 0° C.

FIGURE 5.—Concluded. Effect of side-chain addition on viscosity of 2-alkylbiphenyl and 2-alkylbicyclohexyl hydrocarbons at various temperatures.



(a) Straight-chain substitution.

FIGURE 6.—Effect of temperature on viscosity of 2-alkylbiphenyl and 2-alkylbicyclohexyl hydrocarbons.

In seven out of nine cases, branching the alkyl chain causes a lowering of the boiling point from that of the corresponding straight-chain compound (fig. 4); 2-isopropylbicyclohexyl (high boiling) and 2-*sec*-butylbicyclohexyl (high boiling) are the exceptions in this case. The boiling point of 2-isopropylbicyclohexyl (high boiling) was 0.8° C higher than that of 2-propylbicyclohexyl (high boiling) and the boiling point of 2-*sec*-butylbicyclohexyl (high boiling) was 0.2° C higher than that of 2-butylbicyclohexyl (high boiling).

In figure 5, viscosity is plotted against molecular structure for four different temperatures. In the range of temperatures investigated, branching the alkyl chain increased

the viscosity over that of the corresponding straight-chain compound, except for 2-isopropylbicyclohexyl (high boiling) at two temperatures and 2-isobutylbicyclohexyl (high boiling) at three temperatures. These exceptions involved differences lying practically within the limits of experimental error.

Viscosity of the branched-chain hydrocarbons is plotted against temperature in figure 6 (b). The A. S. T. M. slopes, determined from figure 6 (b), are tabulated in the following table, together with data for the two straight-chain compounds for comparison:

Alkyl substituent	A. S. T. M. slope		
	Biphenyl compound	Bicyclohexyl compound	
		Low boiling	High boiling
2-Isopropyl	1.03	0.92	0.84
2-Propyl	.98	.93	.91
2-*sec*-Butyl	1.04	.94	.87
2-Isobutyl	1.04	.94	.91
2-Butyl	.96	.93	.91

Branching the side chain markedly increased the A. S. T. M. slope of a biphenyl hydrocarbon over its corresponding straight-chain compound. Branching of the alkyl group in the alkylbicyclohexyls causes no marked changes in slope except in the case of the high-boiling isomer of 2-isopropylbicyclohexyl, which showed an unusual drop from 0.91 for the corresponding straight-chain isomer down to 0.84 and a similar decrease from the slope of 2-isopropylbicyclohexyl (low boiling). The high-boiling isomer of 2-*sec*-butylbicyclohexyl showed a somewhat lesser decrease from 0.91 for the straight-chain isomer to 0.87 but also showed a fairly large difference of 0.07 from 2-*sec*-butylbicyclohexyl (low boiling). Of the branched-chain compounds investigated, the high-boiling isomer of 2-isopropylbicyclohexyl shows the least sensitivity of viscosity to temperature and a fairly favorable level of viscosity values.

CONCLUDING REMARKS

Certain pertinent conclusions may be drawn from the results obtained in this investigation with regard to the possible prediction, at least qualitatively, of the physical properties of other members of the series not yet synthesized. In addition, comments may be made as to the suitability of one or more of the hydrocarbons synthesized as high-speed-aircraft fuels.

The effects of changes in molecular structure on physical properties, as pointed out, indicate fairly regular, qualitatively predictable trends for all properties except that of the melting point. The data obtained could not justify even a qualitative prediction of unknown melting points. From the discussion, however, a fairly reliable prediction of the other properties could be made.

With regard to suitability as a fuel, 2-isopropylbicyclohexyl (high boiling) could possibly be selected as the best of the hydrocarbons herein reported on the basis of the properties determined, although there are no great differences among any of the 2-alkylbicyclohexyls. It has a reasonably high heat of combustion per unit volume, while maintaining about the same heat of combustion per unit weight as that of JP-3 fuel. The viscosity-temperature slope is among the lowest of those investigated, and the viscosity values are average for this class of hydrocarbons. The boiling point of 283° C is rather high, but not unreasonably so when compared with the rest of the group. The melting point of −9.13° C is average for this class of compounds and could be lowered considerably by addition of an impurity.

The low-boiling isomer of 2-methylbicyclohexyl also has good viscosity characteristics, that is, relatively low viscosity and a low viscosity-temperature slope. Its melting point, −26.43° C, is the lowest of the compounds investigated and its boiling point, 249.87° C, is the lowest except for bicyclohexyl. Because of the relatively low density, however, its heat of combustion per unit volume is among the lower values and no better than that for JP-3 fuel.

The 2-alkylbiphenyls appear to have the disadvantage of poor viscosity-temperature characteristics, that is, relatively high slopes, and also relatively low values of heat of combustion per unit weight.

The properties discussed herein are by no means the only properties that are significant in evaluating a hydrocarbon for its suitability as an aircraft fuel. These properties have been the sole basis for any evaluation made herein; such factors as carbon-forming tendency, combustion efficiency, ignition, and others have not been considered.

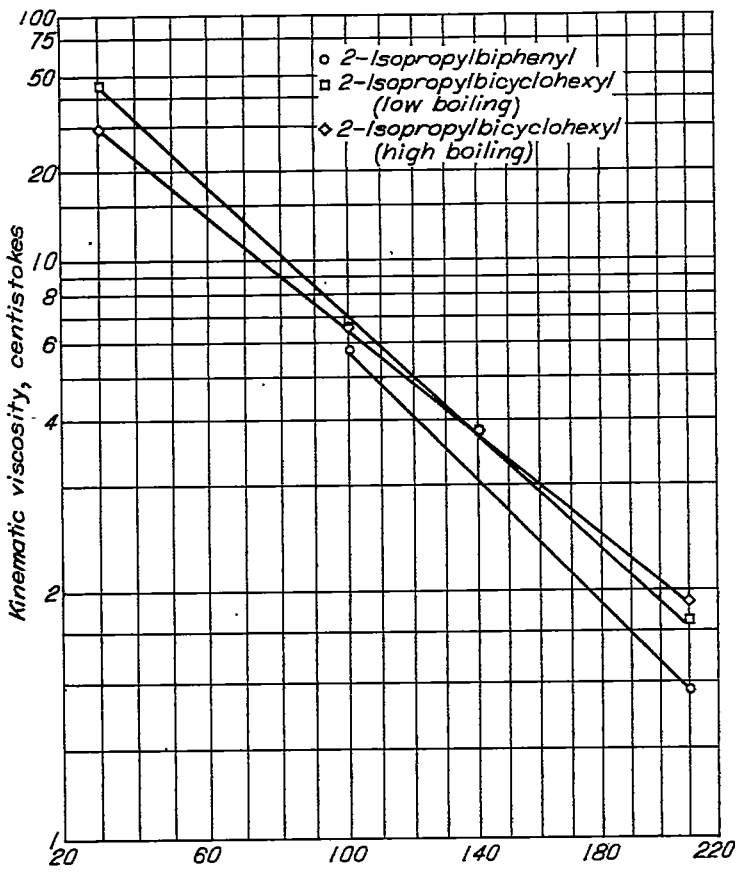
SUMMARY OF RESULTS

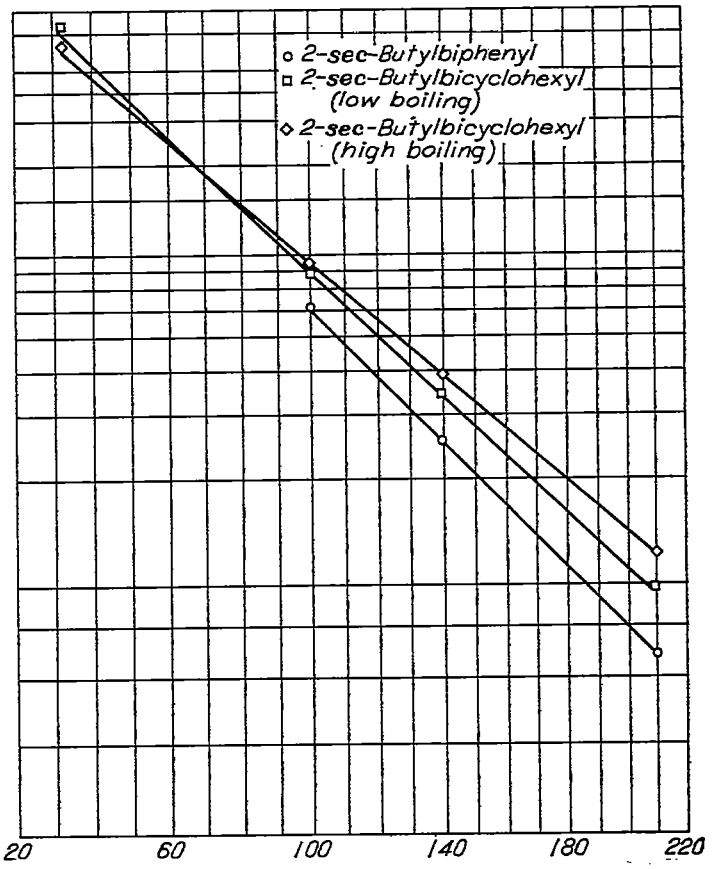
The properties of three homologous series of related dicyclic hydrocarbons were correlated on the basis of their physical properties and molecular structures. The following trends were noted:

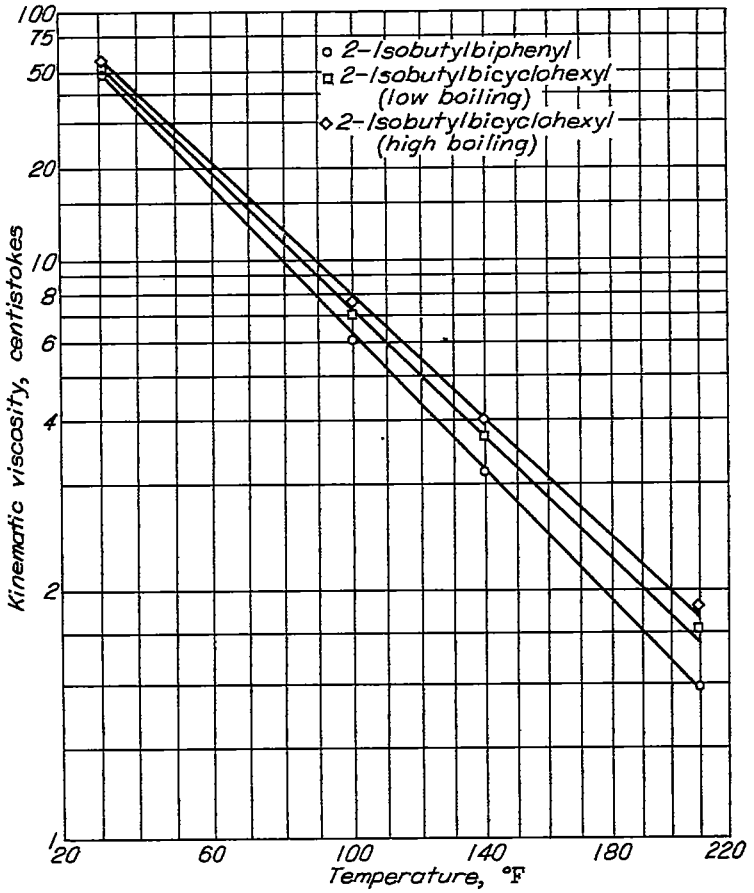
1. The net heat of combustion per unit volume showed average increases of 13 percent for the 2-*n*-alkylbicyclohexyls and 17 percent for the 2-*n*-alkylbiphenyls over the JP-3 fuel value, taken as 911,000 Btu per cubic foot; on a weight basis, the 2-*n*-alkylbicyclohexyls averaged about the same as, and the 2-*n*-alkylbiphenyls averaged 7.6 percent lower than, the JP-3 fuel value, taken as 18,580 Btu per pound. Branching the chain had no appreciable effect on heat of combustion per unit weight but modified the heat of combustion per unit volume in proportion to corresponding density changes. The principal effects noted in heat of combustion on a volume basis are due to density differences.

2. Melting points were progressively lowered for the 2-*n*-alkylbiphenyls with each carbon atom added to the side chain. The 2-*n*-alkylbicyclohexyls (high boiling) showed a less consistent melting-point trend but exceeded the melting points of the corresponding alkylbiphenyls from C_{14} through C_{16}. Branching the chain had no consistent effect on melting point.

3. Boiling points increased regularly with increased chain length, and the boiling points of the 2-alkylbicyclohexyls exceeded those of the 2-alkylbiphenyls from C_{14} through C_{16}. Branching the chain generally lowered the boiling point, except for 2-isopropylbicyclohexyl (high boiling), which boiled 0.8° C higher than 2-propylbicyclohexyl (high boiling), and 2-*sec*-butylbicyclohexyl (high boiling), which boiled 0.2° C above 2-butylbicyclohexyl (high boiling).







(b)

(b) Branched-chain substitution.

FIGURE 6.—Concluded. Effect of temperature on viscosity of 2-alkylbiphenyl and 2-alkylbicyclohexyl hydrocarbons.

4. In all three series, the viscosity increased with each addition of a carbon atom to lengthen the side chain. The viscosities of the 2-alkylbicyclohexyls were higher than those of the corresponding 2-alkylbiphenyls at the temperatures investigated, with the exception of 2-methylbiphenyl at 0° C, which has a viscosity at this temperature higher than those of the corresponding bicyclohexyl compounds because of its greater viscosity-temperature slope.

Branching of the alkyl side chain caused an increase in viscosity over that of the corresponding straight-chain compound, with the exception of 2-isopropylbicyclohexyl (high boiling) at two temperatures and 2-isobutylbicyclohexyl (high boiling) at three temperatures, the latter differences lying practically within the limits of experimental error.

LEWIS FLIGHT PROPULSION LABORATORY
NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS
CLEVELAND, OHIO, *January 25, 1951*

REFERENCES

1. Anon.: Military Specification Fuel; Aircraft Turbine and Jet Engine, Grade JP–3. MIL–F–5624, Jan. 26, 1950.
2. Wise, P. H., Serijan, K. T., and Goodman, I. A.: Correlation of Physical Properties with Molecular Structure for Dicyclic Hydrocarbons Having High Thermal-Energy Release Per Unit Volume. NACA Rep. 1003, 1951. (Formerly NACA TN 2081.)
3. Goodman, Irving A., and Wise, Paul H.: Synthesis and Purification of Some Alkylbiphenyls and Alkylbicyclohexyls. NACA TN 2260, 1950.
4. Glasgow, Augustus R., Jr., Krouskop, Ned C., Beadle, Joan, Axilrod, Gertrude D., and Rossini, Frederick D.: Compounds Involved in Production of Synthetic Rubber. Anal. Chem., vol. 20, no. 5, May 1948, pp. 410–422.
5. Taylor, William J., and Rossini, Frederick D.: Theoretical Analysis of Certain Time-Temperature Freezing and Melting Curves as Applied to Hydrocarbons. RP 1585, Nat. Bur. Standards Jour. Res., vol. 32, no. 5, May 1944, pp. 197–213.
6. Forziati, Alphonse F., Mair, Beveridge J., and Rossini, Frederick D.: Assembly and Calibration of a Density Balance for Liquid Hydrocarbons. RP 1685, Nat. Bur. Standards Jour. Res., vol. 35, no. 6, Dec. 1945, pp. 513–519.
7. Quiggle, D., Tongberg, C. O., and Fenske, M. R.: Apparatus for Boiling Point and Boiling Range Measurements. Ind. and Eng. Chem. (Anal. ed.), vol. 6, no. 6, Nov. 1934, pp. 466–468.
8. Anon.: Tentative Method of Test for Kinematic Viscosity. (Issued 1937; rev. 1938, 1939, 1942, 1946.) A. S. T. M. Designation: D445–46T. A. S. T. M. Standards on Petroleum Products and Lubricants, Nov. 1948, pp. 255–265.
9. Anon.: Standard Method of Test for Thermal Value of Fuel Oil. (Adopted 1919; rev. 1939.) A. S. T. M. Designation: D240–39. A. S. T. M. Standards on Petroleum Products and Lubricants, Nov. 1948, pp. 160–163.
10. Schiessler, Robert W., Herr, C. H., Rytina, A. W., Weisel, C. A., Fischl, F., McLaughlin, R. L., and Kuehner, H. H.: The Synthesis and Properties of Hydrocarbons of High Molecular Weight—IV. Proc. Twelfth Mid-Year Meeting, Div. of Refining, Am. Petroleum Inst. (St. Louis), June 2–3, 1947.

TABLE I—PROPERTIES OF 2-ALKYLBIPHENYL HYDROCARBONS

[S denotes solid at indicated temperature]

Hydrocarbon	Melting point		Boiling point 760 mm		Density at 20° C (g/ml)	Kinematic viscosity [a] (centistokes)				Index of refraction	Net heat of combustion [b]		
	(° C)	(° F)	(° C)	(° F)		98.9° C (210° F)	60° C (140° F)	37.8° C (100° F)	0° C (32° F)	n_D^{20}	(kcal/mole)	(Btu/lb)	(Btu/cu ft)
Biphenyl	69.2	156.6	255.0	491.0	1.041	0.992	S	S	S	S	1445	16,350	1.096×10^6
2-Methylbiphenyl	−.20	31.64	255.30	491.54	1.01134	1.06	----------	3.19	13.27	1.5914	1600	17,100	1.078
2-Ethylbiphenyl	−6.13	20.97	265.97	510.75	.99671	1.17	----------	3.44	13.84	1.5905	1740	17,175	1.069
2-Propylbiphenyl	−11.26	11.73	277.22	531.00	.98018	1.33	----------	4.44	22.41	1.5696	1885	17,300	1.058
2-Butylbiphenyl [c]	−13.71 − 9.65	7.32 14.63	291.20	556.16	.96763	1.43	----------	4.87	24.08	1.5604	2030	17,375	1.048
2-Isopropylbiphenyl	24.46	76.03	269.77	517.59	.98227	1.46	----------	5.76	S	1.5703	1885	17,275	1.060
2-*sec*-Butylbiphenyl	8.12	46.62	281.75	539.15	.97145	1.60	3.52	7.09	S	1.5622	2055	17,575	1.065
2-Isobutylbiphenyl	Glass	----------	282.13	539.83	.96318	1.48	3.17	6.02	48.72	1.5583	2035	17,425	1.047

[a] A. S. T. M. procedure D445–46T.
[b] A. S. T. M. procedure D240–39.
[c] Two crystalline modifications.

TABLE II—PROPERTIES OF 2-ALKYLBICYCLOHEXYL HYDROCARBONS

[S denotes solid at indicated temperature]

Hydrocarbon	Melting point		Boiling point 760 mm		Density at 20° C (g/ml)	Kinematic viscosity [a] (centistokes)				Index of refraction	Net heat of combustion [b]		
	(° C)	(° F)	(° C)	(° F)		98.9° C (210° F)	60° C (140° F)	37.8° C (100° F)	0° C (32° F)	n_D^{20}	(kcal/mole)	(Btu/lb)	(Btu/cu ft)
Bicyclohexyl	3.50	38.30	238.87	461.97	0.88604	1.23	----------	3.07	S	1.4796	1700	18,400	1.017×10^6
2-Methylbicyclohexyl [c]	−26.43	−15.57	249.87	481.77	.88447	1.22	2.08	3.11	8.84	1.4791	1855	18,500	1.022
2-Methylbicyclohexyl [d]	−10.27	13.51	255.00	491.00	.89450	1.51	2.69	4.20	12.85	1.4836	1870	18,650	1.042
2-Ethylbicyclohexyl [c, e]	Glass	----------	266.23	511.21	.89065	1.40	2.58	4.20	16.33	1.4827	1995	18,500	1.027
2-Ethylbicyclohexyl [d]	−.35	31.37	269.54	517.17	.89624	1.54	2.89	4.75	18.53	1.4851	2015	18,650	1.042
2-Propylbicyclohexyl [c, e]	Glass	----------	279.40	534.92	.88527	1.58	3.05	5.38	29.32	1.4807	2145	18,525	1.023
2-Propylbicyclohexyl [d]	.25	32.45	282.22	540.00	.89205	1.71	3.46	6.20	34.08	1.4838	2160	18,675	1.041
2-Butylbicyclohexyl [c, e]	Glass	----------	294.15	561.47	.88227	1.76	3.64	6.74	42.37	1.4799	2300	18,600	1.025
2-Butylbicyclohexyl [d]	−6.51	20.28	296.56	565.81	.88819	1.91	4.05	7.65	51.18	1.4827	2300	18,625	1.032
2-Isopropylbicyclohexyl [c, e]	Glass	----------	277.18	530.92	.89305	1.80	3.75	6.94	46.82	1.4843	2140	18,500	1.031
2-Isopropylbicyclohexyl [d]	−9.13	15.57	283.06	541.51	.90365	1.91	3.79	6.54	29.12	1.4901	2165	18,700	1.054
2-*sec*-Butylbicyclohexyl [c, e]	Glass	----------	290.42	554.76	.89036	1.99	4.38	8.81	82.42	1.4832	2290	18,525	1.030
2-*sec*-Butylbicyclohexyl [d, e]	Glass	----------	296.74	566.13	.90492	2.23	4.82	9.28	63.43	1.4912	2290	18,550	1.048
2-Isobutylbicyclohexyl [c, e]	Glass	----------	286.87	548.37	.87964	1.77	3.68	6.95	51.70	1.4787	2285	18,500	1.016
2-Isobutylbicyclohexyl [d]	13.48	56.26	288.53	551.35	.88658	1.90	4.00	7.53	55.30	1.4819	2295	18,575	1.028

[a] A. S. T. M. procedure D445–46T.
[b] A. S. T. M. procedure D240–39.
[c] Low-boiling isomer.
[d] High-boiling isomer.
[e] Physical properties determined on fractions with most nearly constant density values.